Reactions of Titanium Tetra-chloride and Benzoic Acid

By I. D. VARMA and R. C. MEHROTRA

Summary

The stepwise reaction between titanium tetra-chloride and benzoic acid has been investigated in detail. The formation of $C_6H_5COOTiCl_3$ and $(C_6H_5COO)_2TiCl_2$ is direct and rapid. Further replacement of chlorine by benzoate radical makes the resulting molecule unstable and no tetra-benzoate is formed. A plausible mechanism has been suggested for the decomposition of mono-chloride derivative under different conditions. Titanyl benzoate has been obtained by treating a mixture of titanium tetra-chloride and excess benzoic acid in benzene with anhydrous ammonia. The results indicate that the reactions of titanium tetra-chloride with benzoic acid are similar to those with acetic acid, this finding is in sharp contrast to the different behaviour of titanium tetra-chloride towards alcohols and phenols.

Inhaltsübersicht

Beim Studium der stufenweisen Reaktion zwischen Titantetrachlorid und Benzoesäure wurde festgestellt, daß die Bildung von Benzoyltitantrichlorid oder Dibenzoyltitandichlorid schnell erfolgt. Titanylbenzoat wird bei der Reaktion zwischen Titantetrachlorid und Benzoesäure in Benzol in Gegenwart von wasserfreiem Ammoniak gebildet. Die Ergebnisse deuten auf ähnliche Reaktionen zwischen Titantetrachlorid und Benzoesäure bzw. Essigsäure hin.

Organic compounds of titanium have been receiving considerable attention for some time past. The starting material for the preparation of most of these derivatives is the titanium tetra-chloride and a general feature of the reacions of titanium tetra-chloride with aliphatic hydroxy-compounds[1][2] acetylacetone[3][4][5], and fatty-acids[6] has been shown

[1] J. S. JENNINGS, W. WARDLAW and W. J. R. WAY, J. chem. Soc. London, 637 (1936).

[2] D. C. BRADLEY, W. WARDLAW and D. C. HANCOCK, J. chem. Soc. London, 2773 (1952).

[3] K. C. PANDE and R. C. MEHROTRA, Chem. and Ind. In press.

[4] W. DILTHY, Ber. dtsch. chem. Ges. **37**, 588 (1904).

[5] A. ROSENHEIM, W. LOEWENSTAMM and L. SINGER, Ber. dtsch. chem. Ges. **36**, 1833 (1903).

[6] K. C. PANDE and R. C. MEHROTRA, J. prakt. Chem. [4] **5**, 101 (1957).

to be that the reactions are quite straigth-forward up to the formation of di-chloride derivatives. Compared to alcohols, phenolic compounds have been found to react with titanium tetra-chloride with the formation of titanium tetraphenoxide derivatives[7][8]. In view of the above, it was considered worthwhile to study the reaction between titanium tetra-chloride and benzoic acid also. However, in this case the reaction appears to follow a similar pattern to the reaction betweeen titanium tetra-chloride and acetic acid. When titanium tetra-chloride was caused to react, for a long time, with excess of benzoic acid in refluxing benzene a complex product was obtained which contained the Cl:Ti ratio 0.87, illustrating the complicated nature of the reaction. It is pertinent to point out that the reaction between benzoic acid and zirconium tetra-chloride has been found to yield zirconium tetrabenzoate[9]. Hence it appeared logical to investigate the reaction between titanium tetra-chloride and benzoic acid step-wise.

The reaction between titanium tetra-chloride and benzoic acid (1 and 2 moles) in presence of benzene gave products, directly, corresponding to the following reactions:

$$TiCl_4 + C_6H_5COOH \rightarrow C_6H_5COOTiCl_3 + HCl$$

$$C_6H_5COOTiCl_3 + C_6H_5COOH \rightarrow (C_6H_5COO)_2TiCl_2 + HCl.$$

The products precipitated or crystallised out from benzene as yellow or orange red solids respectively. When the reactants are taken in the molar ratio 1:3 the reaction proceeds slowly after the formation of di-chloride derivative. The mono-chloride $(C_6H_5COO)_3TiCl$ thus formed in refluxing benzene is comparatively unstable and undergoes slow-decomposition as:

$$(C_6H_5COO)_3TiCl \rightarrow (C_6H_5COO)_2Ti{=}O + C_6H_5COCl.$$

This auto-decomposition of mono-chloride derivative is accelerated by heat when other side reactions, also, begin to take place resulting in the formation of a complex end product. One of the plausible side reactions is the formation of benzoic anhydride as under, (cf., reactions of acetyl chloride[1][2]):

$$(C_6H_5COO)_3TiCl + C_6H_5COCl \rightarrow (C_6H_5COO)_2TiCl_2 + (C_6H_5COO)_2O.$$

The correctness of the simple reaction-mechanism suggested above is substantiated by the results of another experiment in which the preparation of titanium tetra-benzoate was attempted by passing anhydrous

[7] H. FUNK, A. SCHLIGEL and K. ZIMMERMANN, J. prakt. Chem. [4], **3**, 320 (1956).
[8] H. FUNK and R. MASTHOFF, J. prakt. Chem. [4], **4**, 35 (1956).
[9] G. JANTSCH, J. prakt. Chem. **115**, 7 (1926).

ammonia in a mixture of titanium tetra-chloride and excess benzoic acid (more than 4 moles) in benzene when the final end-product was found to be titanyl benzoate, $(C_6H_5COO)_2 Ti{=}O$.

Experimental

Apparatus. All glass apparatus with interchangeable joints was used and special care was taken to exclude moisture from all the reactions.

Chemicals. Titanium tetra-chloride (B. D. H.) was purified by redistillation, (b. p. 189.7°/760 mm.).

Benzoic acid (B. D. H., analar) was dried at 40°/1.5 mm. immediately before use.

Analytical methods. Titanium was estimated as di-oxide by ignition of the hydroxide obtained by employing dilute ammonia for precipitation. Chloride was estimated as silver chloride as usual.

Reaction between titanium tetra-chloride and excess benzoic acid

To a clear yellow solution of titanium tetra-chloride (4.85 g.) in benzene (30 g.), benzoic acid (14 g.) was transferred gradually with continous stirring. Large amount of heat was liberated and hydrogen chloride gas escaped freely. The orange coloured solution thus obtained was refluxed for three days nearly, when the evolution of hydrogen chloride gas ceased. A small quantity of solid, which separated on standing, was filtered, washed with benzene and dried at 50°/1.5 mm. Found Ti 15.7%, Cl 10.08%; ratio of Cl:Ti = 0.86.

Reaction between titanium tetra-chloride and benzoic acid. (Molar ratio 1:1)

Benzoic acid (3.3 g.) was added with continuous stirring to a solutions of titanium tetra-chloride (5.02 g.) in benzene (25 g.). The reaction mixture became hot and hydrogen chloride gas evolved freely. A yellow precipitate gradually settled on the bottom of the flask. The reaction mixture was allowed to stand for 12 hours with periodical stirring and was finally freed of hydrogen chloride gas by bubbling into the reaction mixture a current of dry air for eight hours. The yellow precipitate was filtered and washed twice with dry benzene and dried at 60°/1.5 mm. for two hours. A canary yellow micro-crystalline powder (7.2 g.) was obtained. Found Ti 17.38%, Cl 37.63%; Calc. for $C_6H_5COO\ TiCl_3$, Ti 17.38%, Cl 38.17%.

Reaction between titanium tetra-chloride and benzoic acid. (Molar ratio 1:2)

Benzoic acid (3.84 g.) was added with stirring into a solution of titanium tetra-chloride (3.01 g.) in benzene (30 g.). A vigorous reaction ensued with copious evolution of hydrogen chloride gas and separation of a yellow precipitate. The reaction mixture was allowed to stand for 12 hours, after which a current of dry air was admitted through it till all hydrogen chloride gas was removed. An orange solution was obtained, dissolving the initial yellow precipitate. The reaction mixture was concentrated and made free of benzene under reduced pressure (40°/1.5 mm.). The orange residue, thus obtained

was crystallised from benzene in which it is highly soluble. Orange red crystals were separated by decantation and dried at 40°/1.5 mm. (Yield 4.8 g.) Found Ti 13.43%, Cl 18.96%; Calc. for $(C_6H_5COO)_2TiCl_2$, Ti 13.26%, Cl 19.64%.

Reaction between titanium tetra-chloride and benzoic acid. (Molar ratio 1:3)

A current of dry air was sucked through a reaction mixture containing titanium tetra-chloride (2.39 g.), benzoic acid (4.6 g.) and benzene (50 g.) till it became free of hydrogen chloride gas. The resulting orange solution was set aside, for crystallisation, for seven days. The yellow solid which separated, was washed with benzene and dried at 60°/1.5 mm. (Yield 3.8 g.). Found Ti 14.01%, Cl 15.05%, Cl:Ti ratio 1.45; Calc. for a mixture of $(C_6H_5COO)_2TiCl_2$ and $(C_6H_5COO)_2Ti{=}O$ in the molar ratio of 5:2, Ti 13.9%, Cl 14.69%.

Titanium tetra-chloride (4.34 g.), benzoic acid (8.37 g.) and benzene (40 g.) were refluxed for 15 hours at 140°. From the resulting yellow solution, benzene was removed under reduced pressure. The yellow residue was dried at 65°/1.5 mm. A glistening yellow, pungent smelling compound (10.38 g.) was obtained. Found Ti 11.2%, Cl 7.76% (Cl:Ti ratio 0.93). The analysis indicates that the above derivative is mainly $(C_6H_5COO)_3TiCl$ mixed with about 6% $(C_6H_5COO)_2Ti{=}O$, formed by its auto-decomposition.

Above compound (8 g.) was heat for $1^1/_2$ hours at 200°/40 mm. A few drops of colourless, fuming, pungent smelling, mobile liquid collected in the receiver. The residue was refluxed with benzene (15 c.c.) for an hour and allowed to settle for another 12 hours. The supernatant liquor was decanted of and the residue dried at 75°/1.5 mm. A yellow powder (4.5 g.) was obtained. Found Ti 14.21%, Cl 8.37%, (Cl:Ti ratio 0.79). Calc. for a mixture of $(C_6H_5COO)_2TiCl_2$ and $(C_6H_5COO)_2Ti{=}O$ in the molar ratio of 2:3, Ti 14.6%, Cl 8.66%.

Attempted preparation of titanium tetra-benzoate

Anhydrous ammonia was slowly bubbled into a reaction mixture having titanium tetra-chloride (2 g), benzoic acid (5.83 g.) and benzene (40 g) till the solution acquired back the room temperature. The white finely divided suspension, thus obtained, was allowed to settle for 12 hours. The precipitate was filtered and washed with dry benzene. (It contained titanium in traces and was largely ammonium chloride and benzoate.) A faintly yellow crystalline derivative (2.8 g.) was obtained by removing the solvent under reduced pressure and finally drying it at 60°/1.5 mm. Silver nitrate solution produced faint turbidity with the derivative. Found Ti 15.63%. Calc for $(C_6H_5COO)_2Ti{=}O$, Ti 15.66%.

Acknowledgement. One of us (I. D. V.) is grateful to Scientific Research Committee, Uttar Pradesh, for the grant of a scholar-ship during the tenure of which this work was carried out.

Lucknow and Gorakhpur (India), Chemical laboratories, University of Lucknow and Gorakhpur.

Bei der Redaktion eingegangen am 16. September 1958.